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LEWIS ACIDITY OF CARBOXYETHYLTIN CHLORIDES, $Cl_3SnCH_2CH_2CO_2R$ AND $Cl_2Sn(CH_2CH_2CO_2R)_2$

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Summary

The Lewis acidity of estertin chlorides, $Cl_3SnCH_2CH_2CO_2R$ (R = Me, Pr^i, Ph and H) and $Cl_2Sn(CH_2CH_2CO_2R)_2$ (R = Me and Pr^i) has been investigated. Stability constants (K_1, K_2 and K_3) for adducts of these Lewis acids with nitrogen donors, e.g. D = bipy, phen, py, quinoline and aniline, have been determined in CH_2Cl_2 solution at 25 ± 1°C by UV and IR methods. From comparisons of stability constants, the following conclusions can be made: (i) $Cl_3SnCH_2CH_2CO_2Me$ appears as strong a Lewis acid as $MeSnCl_3$ towards bidentate ligands and a single py molecule (from K_1 values); (ii) $Cl_3SnCH_2CH_2CO_2Me \cdot D$ (D = monodentate ligand) is a poorer acceptor than $MeSnCl_3 \cdot D$ but comparable to Me_2SnCl_2 (using K_2 and K_3 values) towards D, and (iii) $Cl_2Sn(CH_2CH_2CO_2R)_2$ is a weaker acceptor than Cl_2SnMe_2 towards phen and bipy (from K_3 values). Qualitatively it was established that for $Cl_3SnCH_2CH_2CO_2R$, the sequence of acidity is R = Ph > Me > Pr^i > H towards bipy. Adducts of $Cl_3SnCH_2CH_2CO_2Me$ and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ with phen and bipy have similar Mössbauer parameters to those for other phen and bipy adducts of organotin trichloride and diorganotin dichloride.

$$RSnCl_3 + D \overset{K_1}{\rightleftharpoons} RSnCl_3 \cdot D$$

$$RSnCl_3 \cdot D + D \overset{K_2}{\rightleftharpoons} RSnCl_3 \cdot 2\ D$$

$$R_2SnCl_2 + D \overset{K_3}{\rightleftharpoons} R_2SnCl_2 \cdot D$$

Introduction

The Lewis acidity of organotin halides has been frequently and variously studied [1]. The majority of the studies have been concerned with complex formation with donor molecules. The dominant concern in these studies has been the investigation of structural and spectroscopic properties of solid adducts. Less attention has been paid to the determination of formation constants of the complexes in solution [1—4]. These data are of value since they are quantitative measures of acceptor strengths and have been used to derive sequences of acceptor ability; e.g. $PhSnCl_3 > Ph_2SnCl_2 > Ph_3SnCl$ towards α,α-bipyridyl (bipy) and also Bu_3P in PhH solution [2], $PhSnCl_3 > MeSnCl_3 > BuSnCl_3$ towards aniline donors in diethyl ether solution [5] and $Ph_2SnCl_2 > Me_2SnCl_2 > Bu_2SnCl_2$ towards pyridine (py) in PhH solution [2]. As exemplified, all these sequences involve simple alkyl- and aryl-tin halides.

While there are many known functionally-substituted organotin halides, few have been studied in regards to their Lewis acidity. When the functional substituent is itself a donor group, e.g. an amine or a carbonyl group, there exists the possibility of intramolecular complexation within the organotin halide. Crystal structure determination have in fact indicated such intramolecular complexations, e.g. in 2-[1-(*S*)-$Me_2NCH(Me)]C_6H_4SnMePhBr$ [6] and the carbonyl-substituted ethyltin chlorides, $Cl_3SnCH_2CH_2CO_2Me$ (I), $Cl_2Sn(CH_2CH_2CO_2Me)_2$ (II), and $Cl_2Sn(CH_2CH_2CONH_2)_2$ [7]. Compound I is a distorted trigonal bipyramid with one chlorine and the coordinated carbonyl oxygen axial while the organic residue and the remaining two chlorines are equatorial; compound II is a distorted octahedron with the two chlorines occupying *cis*-sites and the two organic groups mutually *trans*.

The intramolecular carbonyl coordination is also indicated by the $\nu(CO)$ values, e.g. for I, $\nu(CO)$ is ca. 1660 cm^{-1} and for II $\nu(CO)$ is ca. 1680 cm^{-1}, compared to $\nu(CO)$ = ca. 1740 cm^{-1} for simple esters, such as $MeCO_2Me$ [7—9]. For all carboxyethyltin trichlorides and bis(carboxyethyl)tin dichlorides [8,9] as well as $Cl_2Sn(CH_2CH_2CONH_2)_2$ [7], $X_2Sn(CH_2CH_2COR)_2$, X = Cl, Br or I; R = Ph or alkyl [10], $Me_2ClSn(CH_2)_nCOR$, n = 2 or 3; R = Me or Ph [11] and $Ph_2ClSn(CH_2)_3C(Me)=X$ (X = O or NOH) [12], these is compelling spectral evidence for intramolecular coordination.

Kuivila et al. [11] have shown that an external donor, pyridine, can compete with the carbonyl coordination to the tin centre in $Me_2ClSn(CH_2)_nCOR$ (III). Pyridine coordination to III results in an increase in the $\nu(CO)$ value. Although there appeared to be equilibria involving III and pyridine, no attempt was made to determine the equilibrium constants, nor even the stoichiometry of the adducts.

Poller and Abbas [12] isolated adducts of $X_2Sn[(CH_2)_3COMe]_2$ with bipy; bipy complexation led to increases in the $\nu(CO)$ values (e.g. to 1703 from 1675 cm^{-1} for X = Br). Mössbauer parameters for these adducts suggest similar structures to those of simple dialkyltin dichloride-bipy adducts [13].

We have been studying how such intramolecular coordination affects the Lewis acidity of carboxyethyltin chlorides. As well as the preparation of representative solid adducts, we have looked at equilibria in solution and now report our findings.

Experimental

Carboxyethyltin chlorides, $Cl_3SnCH_2CH_2CO_2R$, R = Me, Ph, Pr^i or H, and $Cl_2Sn(CH_2CH_2CO_2R)_2$, R = Pr^i or Me, were prepared as published [8]. Me_2SnCl_2 was a commercial sample. Analytical data was as expected for all the tin chlorides. Solvents were dried over CaH_2 and distilled before use. Donors were all recrystallised or redistilled commercial samples.

Mössbauer spectra were recorded as previously reported [14].

Determination of equilibrium constants

These were determined from IR or UV data, obtained at 25 ± 1°C in CH_2Cl_2. Solutions were made up and optical cells filled within a dry-box. Absorptions were measured at suitable wavelengths for a number of solutions containing different compositions of a particular acceptor-donor pair; see Table 1 for the wavelengths used. Figs. 1 and 2 illustrate the spectral changes for the bipy-$Cl_3SnCH_2CH_2CO_2Me$ system and in Fig. 3 is shown the IR spectral changes for the $Cl_3SnCH_2CH_2CO_2Me$—py interaction. Concentrations of each donor/acceptor pair were taken to give as great a range of complexation as possible. However for the weaker donors (e.g. anilines) complete complexation could not be achieved. The equilibrium constants were calculated from the absorption data using standard equations [3,5]. In Table 1 are listed the equilibrium constants.

Solid adducts

Solid adducts were prepared by adding hexane dropwise to CH_2Cl_2 solutions containing appropriate molar ratios of the acceptor and donor until

TABLE 1

STABILITY CONSTANTS FOR ADDUCTS OF $Cl_3SnCH_2CH_2CO_2Me$ AND DONORS, D, IN CH_2Cl_2 SOLUTION AT 25 ± 1°C

Donor	pKa	log K_1	log K_2	Wavelength used for measurement (cm^{-1})
Pyridine	5.28	>5	0.8 ± 0.1	ν(CO)
Quinoline	4.90	2.15 ± 0.1		1500
		2.27 ± 0.1	—	[a]
4-$MeOC_6H_4NH_2$	5.36	2.45 ± 0.1	—	[b]
4-$MeC_6H_4NH_2$	5.08	1.85 ± 0.1	—	[b]
$PhNH_2$	4.60	1.50 ± 0.1	—	[b]
Bipy		>5 [c,d]		[a]
α,α'-Biquinolinyl		2.65 ± 0.1 [c]		[b]

[a] $\lambda_{max.}$ of donor and adduct (in UV); [b] $\lambda_{max.}$ of donor (in UV) . [c] Chelate complex; [d] Data did not completely satisfy a simple 1/1 equilibrium.

$K_1 = [Cl_3SnCH_2CH_2CO_2Me \cdot D]/[D][Cl_3SnCH_2CH_2CO_2Me]$

$K_2 = [Cl_3SnCH_2CH_2CO_2Me \cdot 2D]/[D][Cl_3SnCH_2CH_2CO_2Me \cdot D]$

K_A = dissociation constants of DH^+ in water at 25°C.

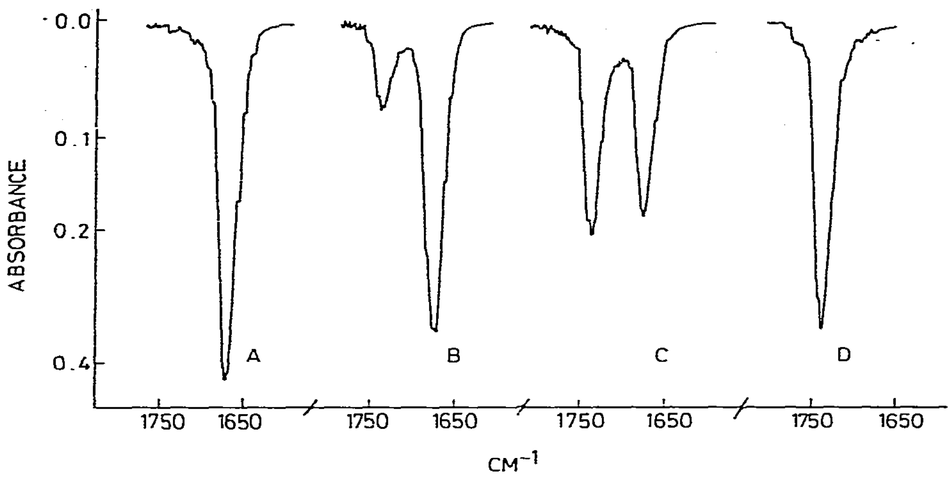


Fig. 1. Infra-red spectra in the carbonyl region for bipy—$Cl_3SnCH_2CH_2CO_2Me$ interaction in CH_2Cl_2 solution at 25 ± 1°C. [$Cl_3SnCH_2CH_2CO_2Me$] = 1.44×10^{-2} *M*; [bipy] = 0, (A), 0.288×10^{-3} *M* (B); 0.86×10^{-3} *M* (C); 1.44×10^{-2} *M* (D).

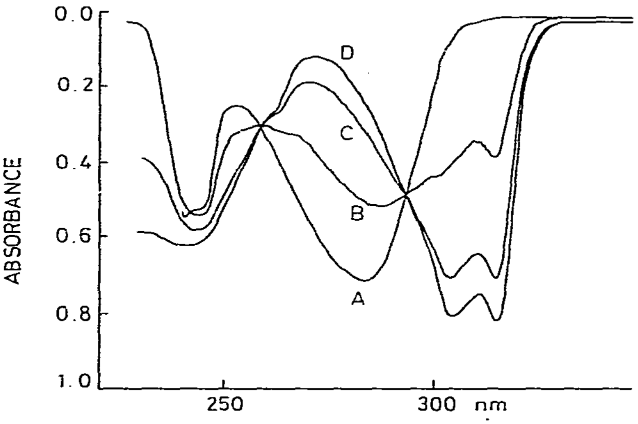


Fig. 2. UV spectra for the bipy—$Cl_3SnCH_2CH_2CO_2Me$ interaction in CH_2Cl_2 solution at 25 ± 1°C. [bipy] = 5×10^{-5} *M*; [$Cl_3SnCH_2CH_2CO_2Me$] = 0, (A); 2.5×10^{-5} *M*, (B); 5×10^{-5} *M*, (C); 10×10^{-5} *M* (D).

TABLE 2

ANALYTICAL AND OTHER DATA FOR CARBOXYETHYLTIN CHLORIDE COMPLEXES

Compound	Analysis calc. (Found) (%)				m.p. (°C)	ν(CO) (KBr) (cm^{-1})
	C	H	Cl	N		
$MeO_2CCH_2CH_2SnCl_3$ · bipy	35.9 (35.7)	3.2 (3.1)	22.7 (23.0)	6.0 (5.8)	203—206	1728
$MeO_2CCH_2CH_2SnCl_3$ · phen	39.1 (39.5)	3.1 (3.1)	21.6 (21.3)	5.7 (5.5)	198—200	1725, 1735, [a] 1745
$(MeO_2CCH_2CH_2)_2SnCl_2$ · bipy	41.6 (41.9)	4.3 (4.2)	13.6 (13.4)	5.4 (5.2)		1728
$(MeO_2CCH_2CH_2)_2SnCl_2$ · phen	44.2 (44.4)	4.1 (3.9)	13.0 (12.9)	5.2 (5.3)	139—142	1720 [a] 1730 1750

[a] Samples recrystallised from CH_2Cl_2/hexane solutions.

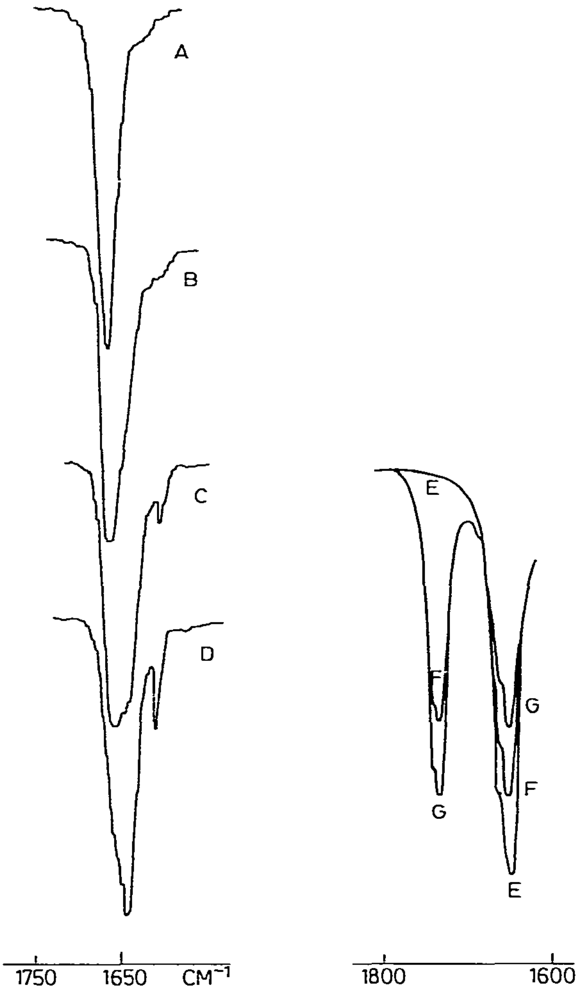


Fig. 3. Infra-red spectra in the carbonyl region for pyridine—$Cl_3SnCH_2CH_2CO_2Me$ interaction in CH_2Cl_2 solution at 25 ± 1°C. [$Cl_3SnCH_2CH_2CO_2Me$] = 1.55 × 10^{-2} *M*, [pyridine] = 0 (A); 0.389 × 10^{-3} *M* (B); 0.778 × 10^{-3} *M* (C) and 1.55 × 10^{-2} *M* (D). [$Cl_3SnCH_2CH_2CO_2Me$] = 2.64 × 10^{-2} *M*; [pyridine] 2.64 × 10^{-3} *M* (E); 10.6 × 10^{-3} *M* (F); 16.0 × 10^{-3} *M* (G).

precipitation resulted. Recrystallisations were attempted from hexane/CH_2Cl_2. Analytical and other data for bipy and phen complexes are given in Table 2.

Results and discussion

Solid complexes of I and II with bidentate ligands, such as bipy and phen, were the easiest to prepare. Mössbauer data for these compounds are given in Table 3. Also included in Table 3 are published data for $BuSnCl_3$ [15,16], Oct_2SnCl_2 [15] and $Br_2Sn(CH_2CH_2CH_2COMe)_2$ [12] complexes. For all the $RSnCl_3$ complexes [R = Bu and $MeO_2CH_2CH_2$ as well as Ph], a common structure is suggested from the similar Mössbauer parameters. Mullins [16] proposed octahedral structures with two chlorides mutually *trans* for

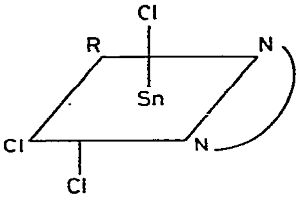
TABLE 3

TIN—119m MÖSSBAUER PARAMETERS FOR CARBOXYETHYLTIN CHLORIDE AND THEIR COMPLEXES [a] AND COMPARISON WITH LITERATURE VALUES FOR SIMPLE ALKYLTIN CHLORIDE ANALOGUES

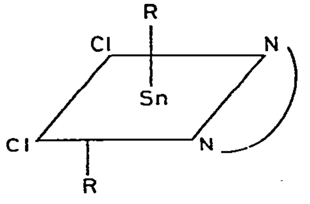
Compound	I.S. [b]	Q.S. [b]	Ref.	Compound	I.S. [b]	Q.S. [b]	Ref.
$Cl_3SnCH_2CH_2CO_2Me$	1.08 [c]	2.04 [c]	This work	$Cl_2Sn(CH_2CH_2CO_2Me)_2$	1.45 [d]	3.47 [d]	This work
$Cl_3SnCH_2CH_2CO_2Me \cdot$ bipy	0.85	1.59	This work	$Cl_2Sn(CH_2CH_2CO_2Me)_2 \cdot$ bipy	1.46	3.93	This work
$Cl_3SnCH_2CH_2CO_2Me \cdot$ phen	0.93	1.65	This work	$Cl_2Sn(CH_2CH_2CO_2Me)_2 \cdot$ phen	1.50	3.93	This work
$BuSnCl_3$	1.37	1.95	[15]	Oct_2SnCl_2	1.68	3.74	[13]
	1.38	1.86	[16]	$Oct_2SnCl_2 \cdot$ bipy	1.59	4.00	[13]
				$Oct_2SnCl_2 \cdot$ phen	1.56	4.11	[13]
$BuSnCl_3 \cdot$ bipy	1.01	1.66	[15]				
	0.87	1.62	[16]	$Br_2Sn(CH_2CH_2COMe)_2$	1.66	3.83	[12]
				$Br_2Sn(CH_2CH_2COMe)_2 \cdot$ bipy	1.56	3.80	[12]
$BuSnCl_3 \cdot$ phen	1.03	1.67	[15]				
	0.91	1.60	[16]				

[a] Recorded at 77 K vs. a $CaSnO_3$ source at ambient temperature. [b] mm/sec. [c] Literature values I.S. 1.00, Q.S. 2.18 [7]; I.S. 1.35 Q.S. 2.00 [9]. [d] Literature values I.S. 1.50, Q.S. 3.45 [7]; I.S. 1.35, Q.S. 3.45 [9].

$RSnCl_3 \cdot L{-}L$ (IV), R = Bu or Ph, L—L = phen or bipy, and this must be considered also for IV, R = $CH_2CH_2CO_2Me$. All $R_2SnX_2 \cdot L{-}L$ (V) (R, X = Me, Cl [4,17] Oct, Cl [15] and $MeCOCH_2CH_2CH_2$, Br [12]) have similar Mössbauer parameters (and hence structures) to those of V, (R, X = $MeO_2CCH_2CH_2$, Cl). The quadrupole splittings values ca. 4 mm/sec, are those expected, from point-charge calculations [18], for octahedral complexes with *trans*-R_2Sn groups.



(IV)



(V)

Complexation of I and II by these chelating ligands frees the carbonyl groups and results in the expected increases in ν(CO) (Table 2). The phen adducts of both I and II, when obtained from CH_2Cl_2/hexane solutions, gave three carbonyl maxima as indicated in Table 2, yet only one ν(CO) was found for the adducts obtained from PhH/CH_2Cl_2 solution [e.g. for phen-I, ν(CO) 1738 cm^{-1}]. We assume that these carbonyl absorptions are due to different conformations. The bipy adducts, on the other hand, consistently gave just one absorption.

Adducts of II and related diestertin dichlorides with monodentate ligands could not be isolated. Even adducts of monodentate ligands with I proved difficult to isolate in a pure state, e.g. attempts to crystallise crude $Cl_3SnCH_2CH_2CO_2Me \cdot py$ (initially precipitated from a CH_2Cl_2 solution containing a 1/1 mole ratio of components by addition of hexane) led to the breakdown of the complex and recovery of I.

IR spectra in CH_2Cl_2 solutions

For many donors, there were IR spectral indications for interactions with I and II in CH_2Cl_2 solution, even if solid adducts could not be obtained, see Table 4.

The chelating ligand, $Ph_2P(O)CH_2(O)PPh_2$, as well as bipy and phen, clearly complexes strongly and practically completely with I. This is borne out by ν(CO) for solutions containing equimolar donor and I, being at ca. 1730 cm^{-1} with negligible absorption at 1670 cm^{-1}. Several monodentate ligands, e.g., pyridine, quinoline, $(MeO)_3P$ and Me_2SO, also coordinate to I strongly, if not all completely at a 1/1 ratio of components, to give hexacoordinate tin, e.g. VI and VII. The carbonyl group is still coordinated to tin as shown by the ν(CO) values. The 1/1 complexation by these monodentate ligands causes slight shifts (decreases) in ν(CO) as well as decreases in E_A as compared to values in I. Such changes, albeit small, can be used diagnostically for 1/1 complexation *. The small shifts in ν(CO) indicate little changes in the character of the

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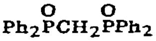
* Confirmation of complexation can be gained from other spectral changes, e.g. for the quinoline interaction, decrease in the absorption at 1500 cm^{-1} and for the Me_2SO interaction development of new absorption at 990 cm^{-1} [complexed ν(SO)].

TABLE 4

CARBONYL FREQUENCIES AND INTENSITIES FOR MIXTURES OF $Cl_3SnCH_2CH_2CO_2Me$ (A) AND DONORS (D) IN CH_2Cl_2 SOLUTION AT 25 ± 1°C

Donor	[A]/[D]	ν(CO) (cm^{-1})	$E_A \times 10^{-2}$ [a]	Comments
—	1/0	1668	5.6	—
Ph_3P	1/1	1667	5.3	No interaction
$(MeO)_3P$	1/1.5	1668	4.3	1/1 Complexation; carbonyl group still coordinated
 $Ph_2\overset{O}{P}CH_2\overset{O}{P}Ph_2$	1/1	1730	4.3	Chelate complex, carbonyl free
Ph_3AsO	1/1	1665	4.85	Slight interaction
Me_2CO	1/1.4	1670	5.4	No interaction
Me_2SO	1/5	1660	3.7	1/1 and 1/2 complexes
		1725	0.6	
Quinoline	1/1	1665	4.3	1/1 complex
phen	1/1	1733	4.35	Chelate complex
bipy	1/1	1730	4.65	Chelate complex
py	1/1	1648	4.3	1/1 complex
	1/14	1730	4.5	1/2 complex

[a] E_A = apparent molecular absorption coefficient.

C=O bond as the additional ligand complexes with the tin centre. In going from the five-coordinate I to the six-coordinate adduct, e.g. VI and VII, one might assume, in the absence of other effects, that ν(CO) should increase [towards the ν(CO) value for a free carbonyl group], since the $>C{=}O \rightarrow Sn$ interaction should be reduced and as a consequence greater double bond character in the carbonyl bond would result. However this is not so and some compensating effect must operate. This compensating effect could be back bonding from tin to oxygen (using the carbonyl anti-bonding orbital) as the additional ligand complexes. An additional cause could be the structural change in going from I (trigonal bipyramidal) to VI and VII (octahedral).

For the more powerful monodentate donors (D), e.g. pyridine and Me_2SO, addition of donor beyond a 1/1 mole ratio leads to adducts of 2(D)/1(I) stoichiometries and development of ν(CO) at ca. 1730 cm^{-1}.

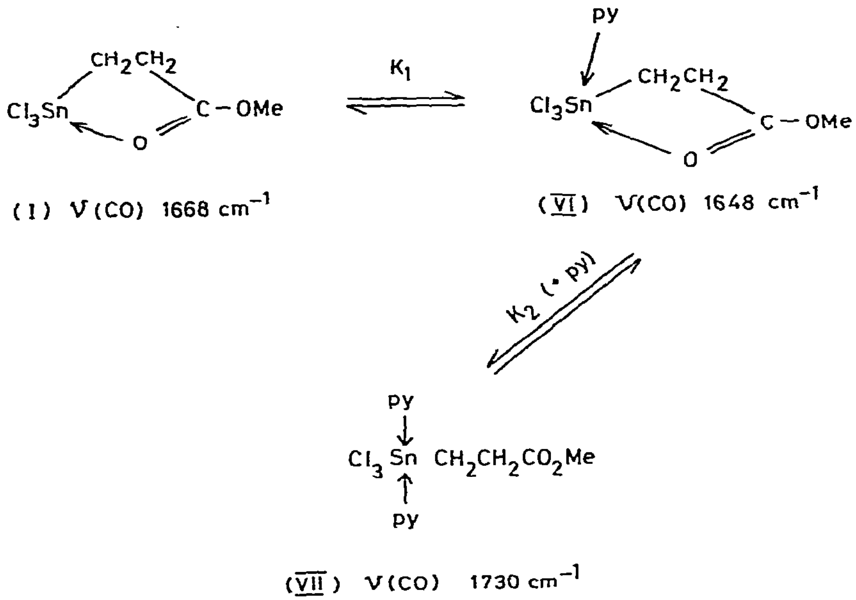
Equilibrium constants

Equilibrium constants are listed in Table 1. The major study was made with I.

Complexation by pyridine, as discussed earlier, occurs in two stages (Scheme 1). However the first pyridine complexes too strongly for accurate measurement. A lower estimate for log K_1 would be 5. The second equilibrium constant K_2 was more accessible.

In Table 5, are listed published equilibrium constants for organotin chloride—pyridine interactions. From the data, it is possible to compare the relative acidities of I, $RSnCl_3$ (R = Bu or Ph) and R_2SnCl_2 (R = Me or Bu) towards pyridine. The data has been gathered in different solvents, namely PhH, CCl_4 and CH_2Cl_2. However little differences are to be expected for log K_1 values

SCHEME 1



obtained in these non-coordinating solvents. The temperature differences can also be ignored and so the log K_1 values can be compared without amendment.

Satchell and coworkers [19] reported that the log K_1 for the 1/1 3,5-dichloropyridine/$PhSnCl_3$ complex in Et_2O solution was 0.92. From the pK_a values of 3,5-dichloropyridine (0.76) and pyridine (5.28), one can estimate the log K_1 value for $PhSnCl_3$-py to be at least 5 in Et_2O and certainly also in CH_2Cl_2.

The intramolecular coordination in I cannot increase the electron density too much on tin as this would lead to a very significant difference in the Lewis acidities of I and $PhSnCl_3$ towards a monodentate donor. Different reorganisation energies for $PhSnCl_3$ and I on complexation (i.e. due to changes in hybridisation and structures) could have some influence. That no intramolecular complexation has to be undone in I on order to accommodate the first pyridine molecule also must be important. When such intramolecular complexation has to be removed, as happens when the second pyridine complexes to I, the log K_2 value is considerably reduced. From the data, the acidity of MeO_2-

TABLE 5

COMPARISON OF STABILITY CONSTANTS FOR PYRIDINE-ORGANOTIN CHLORIDE (A) ADDUCTS

R_nSnCl_{4-n}	log K_1	log K_2	log K	Solvent/Temp (°C)	Ref.
Me_3SnCl	0.28			PhH/30	25
				CCl_4/27	26
Me_2SnCl_2	1.23	1.11		PhH/30	2
Bu_2SnCl_2	0.80	0.70		PhH/30	2
$MeO_2CCH_2CH_2SnCl_3$	>5	0.85		CH_2Cl_2/25	This work
$BuSnCl_3$			>5.6	PhH/30	2

$K_1 = [A \cdot py]/([py][A])$; $K_2 = [A \cdot py_2]/[A \cdot py][py]$; $K = [A \cdot py_2]/[A][py]^2$

$CCH_2CH_2SnCl_3 \cdot py$ appears only comparable to that of $R_2SnCl_2 \cdot py$ (R = Me or Bu).

The log K_1 values for the aniline adducts enabled comparison of acidities of I and $PhSnCl_3$ towards another type of monodentate ligand, anilines, to be made. The aniline interactions were followed by UV spectroscopy. As observed for other tin halide—aniline interactions [5,21] weak long-wavelength charge-transfer absorption was observed for the adducts. Complete 1/1 complexation was not achieved even with the maximum concentration of I used and hence $\lambda_{max.}$ for the charge-transfer absorption could not be determined with any accuracy; under the conditions used, [I] > [D], adducts of stoichiometries 2D/1I were not expected.

Correlations have been established between pK_a for anilines and log K_1 for aniline-$PhSnCl_3$ complexes in ether at 23°C [5] (eq. 1) and in dioxane at

$$\log K_1 = 0.80\ pKa - 1.40 \tag{1}$$

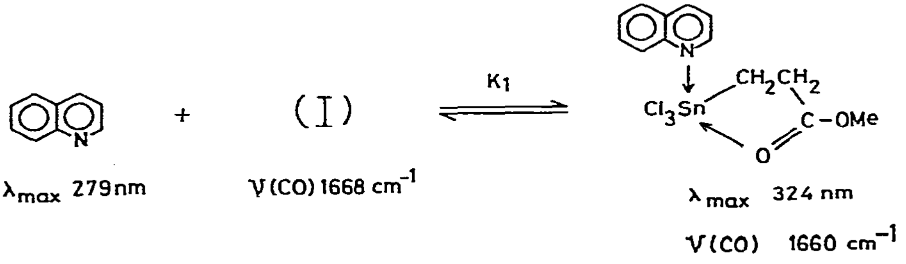
$$\log K_1 = 0.79\ pKa - 0.94 \tag{2}$$

25°C [20] (eq. 2). Satchell and coworkers [20] actually measured the log K_1 value (= 2.68) for the $PhSnCl_3$-$PhNH_2$ complex in dioxane at 25°C. This value and those calculated from the correlations are listed below:

	log K_1	log K_1
$PhNH_2$-$PhSnCl_3$	2.28 (Et_2O)	2.68 (dioxane)
4-$MeC_6H_4NH_2$-$PhSnCl_3$	2.66 (Et_2O)	3.09 (dioxane)
4-$MeOC_6H_4NH_2$-$PhSnCl_3$	2.89 (Et_2O)	3.29 (dioxane)

Some differences in log K_1 values in ether and in non- or weakly coordinating solvents such as CH_2Cl_2 are generally to be expected. For example, for $SnCl_4$ complexes, K_1 values in Et_2O are ca. 40 times less than in *o*-dichlorobenzene. For the weaker acceptor, $SnBr_4$, the difference reduces to 3 times [22]. It is anticipated that for the still weaker Lewis acid, $PhSnCl_3$ [5] the differences between K_1 values in Et_2O and non-coordinating solvents (e.g. CH_2Cl_2) should be small. With this in mind, we conclude that the acidity difference between $PhSnCl_3$ and I towards aniline bases is between 2—5 times. Furthermore, the relative acidity sequence of $PhSnCl_3$/$MeSnCl_3$/$BuSnCl_3$ was established as 12/3/1 [5] and so, for example, I has a comparable acidity to that of $MeSnCl_3$ towards anilines.

The quinoline—I interaction (eq. 3) was studied both by UV and IR spectro-



(3)

scopies. Similar UV spectral changes as reported by Satchell [19] for other quinoline-Lewis acid systems were observed. Only the 1/1 adduct was indicated. Despite the quite different concentrations used — for the UV study [quinoline] 2.11×10^{-4} M and [I] 0.75—75×10^{-4} M and for the IR study [quinoline] 4.22×10^{-2} M and [I] 4.24—42.4×10^{-3} M — consistent log K_1 values were calculated.

It has been reported [19] that pyridines are 30—50 fold and quinolines 2—20 fold more basic towards Lewis acids such as $SnCl_4$ and $ZnCl_2$, than expected compared with an aniline of similar p*K*a value. Towards I, the relative basicities of pyridine (p*K*a 5.28), quinoline (p*K*a 4.90) and aniline (p*K*a 4.60) are 3000/5/1. Thus for I, a fairly elaborate Lewis acid, a similar trend is found for aniline and quinoline, although pyridine appears to be much more basic.

Bipy proved to be a considerably stronger chelating ligand than α,α-biquinolyl. Unfortunately the log K_1 value for bipy-I was too great (>5) to allow accurate calculation. In addition, it appears as if a simple 1/1 equilibrium did not completely satisfy the data. On a qualitative basis, a sequence of acceptor ability of $Cl_3SnCH_2CH_2CO_2R$ towards bipy [$R = Ph > Me > Pr^i > H$] was obtained. This sequence was established from the amounts of uncomplexed donor in solutions containing equimolar donor and acceptor. The UV spectral changes on complexation of bipy (see Fig. 2) are similar to those recorded for complexation by other organotin halides [3,23,24]. Various bipy-organotin halide formation constants have been reported (Table 6) and hence comparison of acidity towards bipy can be made. These data show that even to a chelating donor, I has a comparable acidity to $RSnCl_3$.

Equilibrium constants for $Cl_2Sn(CH_2CH_2CO_2R)_2$ *adducts.*

Comparison of the Lewis acidities of $Cl_2Sn(CH_2CH_2CO_2R)_2$ and Me_2SnCl_2 can be made towards two donors. From data in Table 6, Me_2SnCl_2 is ca. 200 times more acidic than $Cl_2Sn(CH_2CH_2CO_2Pr^i)_2$ towards bipy and from data

TABLE 6

COMPARISON OF STABILITY CONSTANTS FOR α,α-BIPYRIDYL ADDUCTS WITH ORGANOTIN HALIDES

R_nSnCl_{4-n}	log K_1	Solvent/Temp (°C)	Ref.
Me_2SnCl_2	2.09	PhH/30	2
	3.42, 3.30	MeCN/25	4, 23
	3.55	CH_2Cl_2/25	This work
Bu_2SnCl_2	1.60	PhH/30	2
	3.03	MeCN/25	23
Oct_2SnCl_2	1.43	PhH/30	3
Ph_2SnCl_2	3.80	PhH/30	2
$(Pr^iO_2CH_2CH_2)_2SnCl_2$	1.2	CH_2Cl_2/25	This work
$BuSnCl_3$	5.0	PhH/30	2
	>7.0	MeCN/25	23
$PhSnCl_3$	>5.0	PhH/30	2
$MeO_2CCH_2CH_2SnCl_3$	>5.0	CH_2Cl_2/25	This work

$K_1 = [(R_nSnCl_{4-n}) \cdot bipy]/[R_nSnCl_{4-n}][bipy]$

TABLE 7

STABILITY CONSTANTS FOR R_2SnCl_2-phen COMPLEXES

	log K_1	Solvent/Temp (°C)	Ref.
$Cl_2Sn(CH_2CH_2CO_2Pr^i)$-phen	2.10 ± 0.10	$CH_2Cl_2/25$	This work
Me_2SnCl_2-phen	5.67	$CH_3CN/25$	4

$K_1 = [R_2SnCl_2phen]/[R_2SnCl_2][phen]$.

in Table 7, a greater factor ($>3 \times 10^3$) can be estimated for the difference between Me_2SnCl_2 and $Cl_2Sn(CH_2CH_2CO_2Me)_2$ towards phen.

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